Visible light emitting devices with Schottky contacts on silicon nanocrystals

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We have fabricated light emitting diodes (LEDs) with Schottky contacts on Si-nanocrystals formed by simple techniques as used for standard Si devices. Orange electroluminescence (EL) from these LEDs could be seen with the naked eye at room temperature when a reverse bias voltage was applied. The EL spectrum has a major peak with a photon energy of 1.9 eV and a minor peak with a photon energy of 2.2 eV. Since the electrons and holes are injected into the radiative recombination centers related to nanocrystals through avalanche breakdown, the voltage needed for a visible light emission is reduced to 4.0 - 4.5 V, which is low enough to be applied by a standard Si transistor.

There have been expectations that high-efficiency light emitting diodes (LEDs) using silicon-(Si-) related materials can be realized for monolithic optoelectronic integrated circuits (ICs). Various types of LED based on Si-related materials have been tried to date. Of Si-related materials investigated, porous Si (PS) has been studied most actively. The quantum efficiency and stability of LEDs based on PS have been gradually improved. [1] Recently, Si nanocrystals (Si-NC) have also been studied for their light-emitting characteristics. Si-NCs can be formed using methods which fit in better with standard silicon technology as compared with PS, since electrochemical processes are not needed. Based on the previous studies, it is predicted that the optical band gap is increased [2] and the probability of radiative recombination for excitons is enhanced [3] with a decrease in the size of nanocrystals owing to the quantum confinement effect. Significant increases in oscillator strength are also predicted at the very small dimensions of NCs. [4] Visible photo-luminescence (PL) with high efficiency has been reported with Si-NCs formed by various methods: chemical vapor deposition using silane or disilane gas resolved by microwave plasma, [5] laser [6], or thermal reactions; [7] ion implantation of Si into silicon oxide films followed by post-annealing; [8] and crystallization of amorphous Si (a-Si) films. [9] The reported photon energy of the PL peak spectra is 1.5 to 1.9 eV (red) for most Si-NCs. Blue PL emission with a peak photon energy of 3.2 eV has also been obtained from Si-NCs formed by crystallization of amorphous Si films. [9] The luminescence related to defects in SiO2 with a peak photon energy more than 2 eV has also been reported. [8] The number of the reports on electroluminescence (EL) from the LEDs [10] [11] [12] is very small as compared with that for PL from Si-NCs. This is principally because the carrier injection induced electrically is more difficult than that induced optically. In the investigations reported, visible EL was obtained from Si-NCs in SiO2 matrix formed by chemical vapor deposition (CVD) [10] or by Si+-implantation into SiO2; [11] and from a multi-quantum-well (MQW) composed of silicon-nitride(SiNx)/Si-NC formed by plasma enhanced CVD and laser annealing. [12] The EL in these cases was strong enough to be seen with the naked eye. These results indicate that there is promise in using Si-NCs to re-

alize LEDs based on Si-related materials. However, as yet the operating voltage is still rather high (10 25 V or more) for the devices to be driven by standard Si-ICs. This is because the Si-NCs in these cases are sandwiched between insulating layers or embedded by insulating layers, through which the carriers must pass by direct tunneling. This high voltage must be reduced in order to use LEDs based on Si-NCs practically. A simple structure which can be fabricated easily by standard Si-IC technology is also desired for the LED. In this study, we have fabricated simple LEDs with Schottky contacts on Si-NCs and without the insulating layers. Visible EL has been observ ed form this LED. The EL is strong enough to be seen with the naked eyes at room temperature and with a relatively low operating voltage. The Si-NCs were formed as follows by the crystallization of a-Si . The p-type Si wafer had a diameter of 150 mm and low resistivity (0.01 ohm cm). The native oxide was removed by etching before the deposition of a-Si. A molecular beam of Si, formed by resolving disilane using a tungsten cracking heater, [13] was deposited onto the Si substrate at room temperature. The a-Si was converted into nanocrystals by rapid heating to 700 degree C for one or three minutes in pure oxygen gas. During this heating, oxidation of silicon occurs simultaneously. The oxidation is effective to stabilize the surface. It was known in advance that the thickness of oxide formed on a crystalline Si substrate for one and three minutes of oxidation was about 0.5 and 0.7 nm, respectively, in the oxidation furnace used. PL measurements for these samples were performed using the Ar+ laser (458nm) at room temperature. The structure of these samples was observed using a high-resolution transmission electron microscope (HR-TEM). Metal contacts composed of titanium and gold (Ti/Au) were formed by electron beam (EB) evaporation on the back of the substrate. Ti/Au contacts 100 x 100 mm2 in area were formed on the surface of the Si-NCs by the lift-off process. Device isolation was not employed. Figure 1 shows a cross-sectional scheme of the resulting device. For reference, p-type Si substrates were also annealed in oxygen gas and the devices with Schottky contacts were fabricated on them. The current-voltage (I-V) characteristic was measured at room temperature. EL was measured at room temperature using a monochrometer and a photomultiplier. At room temperature, the PL signal with peak photon energy of 1.9eV was obtained from the a-Si layers that experienced one minute of oxidation. On the other hand, there were no detectable PL signals from either the a-Si layers without annealing or the samples that experienced three minutes of oxidation. Figure 2 shows a cross-sectional HR-TEM lattice image of an a-Si layer that experienced one minute of oxidation. Tiny Si-nanocrystal islands of almost hemispherical shape and 2-3 nm wide are seen in the a-Si layer. The presence of stacking faults between the islands and the substrate indicates that the islands did not exist prior to deposition of the a-Si layer. It is possible that the other nanocrystals of dimensions less than about 2nm was formed in a-Si layer,

since lattice image of such small crystals can hardly be obtained even by HR-TEM. The surface of the a-Si layer may be oxidized, though the oxide layer cannot be distinguished from the a-Si layer owing to the low contrast between the two in the TEM image. A previous report indicates that 2-3nm rectangular-shaped nanocrystals were formed by a similar method and that strong blue PL was observed. [14] In the case of a-Si layers that experienced three minute of oxidation, it was reveled that most of the a-Si was converted into large crystals of Si, whose surface was slightly oxidized . Thus, it was founded that the origin of PL was related to the formation of Si-NCs. The I-V characteristics of these Si-NC devices show rectifying behavior. Figure 3 shows a typical I-V characteristic measured for a device that experienced one minute of oxidation. Devices which experienced three minutes of oxidation exhibited smaller forward and reverse currents. The I-V characteristic of each device was stable and changed little after repeated measurements. Orange EL emissions from Si-NC devices that experienced one minute of oxidation were clearly seen with the naked eye at room temperature when a reverse bias voltage was applied. The critical reverse current for the observation of light emission with the naked eye was 30 to 40 mA at an applied voltage of 4.0 to 4.5V. In contrast, it was not possible to obtain visible EL emissions from either Si-NC devices that experienced three minute of oxidation or the reference devices without a-Si layers at room temperature. These results indicate that the visible EL is related to the existence of Si-NCs formed in a-Si . Figure 4 shows a typical EL spectrum for a Si-NC device. This spectrum was measured at room temperature under a reverse bias of 5.0V and at a current of 60 mA. Two peaks are visible. The peak wavelength, equivalent photon energy and full-width at half-maximum (FWHM) are 650 nm, 1.9 eV and 110 nm for the major peak (peak A), and 570 nm, 2.2 eV and 30 nm for the minor peak (peak B), respectively.The FWHM of the major peak (peak A) is relatively small as compared with that of a PS EL spectrum. [15] The peak wavelength and FWHM of the main peak is close to that obtained from a multi-quantum well (MQW) of (SiNx)/Si-NC. [12] In the report of this MQW, it is thought that the orange EL is due to radiative recombination between the states quantized by the quantum confinement at the Si-NCs. For the tiny Si-nanocrystal islands seen in the TEM image of Fig.2, their structure may be not effective for the quantum confinement. However, in the case that nanocrystals which are invisible in this TEM image are formed in SiOx near the surface, the quantum confinement is possible. In contrast, it has been reported that the red PL (1.5-1.9eV) in the case of the oxidized Si-NC particles [5] [6] [7] is due to the localization of excitons or carriers at the Si/SiOx interface. [16] The peak energy for peak B (2.2eV) is close to that for PL spectrum of oxidized Si-NC particles reported in another article; [17] where its origin seems to be Si/SiOx interface states; however, the details are unknown. In order to clarify the origin of these EL peak

s, it is necessary to examine the details of luminescence such as temperature dependence of both peak energy and peak intensity, the size dependence of peak energy, and the time-resolved characteristics of light emission. These will be studied in the near future. Although the origin of EL is unclear at this stage, it is evident that these light emissions are deeply related to the formation of the Si-NCs. It should be noted that the spectrum shown in Fig.4 is quite different from that produced by a reverse-biased p-n junction of silicon, where the spectrum spans the entire visible range and the emitted light is white. [18] The observation that EL is emitted only under reverse bias is unique. Though similar characteristics have been obtained for a LED based on germanium-NCs embedded in SiO2, [19] such behavior is quite different from that reported in the past for those on PS or Si- NCs. EL was obtained when avalanche breakdown occurred, as shown in Fig.3, where the electrons and holes that were produced by impact ionization have enough energy to be injected into the emission centers at NCs. On the contrary, when under forward bias, the injection of carriers into these levels is impossible, since the energy of carriers outside the nanocrystals is low. Since avalanche breakdown easily occurs in our devices even with a low bias voltage, the operation voltage for visible EL can be reduced to 4.0 to 4.5 V, which is so low that these diodes can be driven by a standard Si bipolar transistor. It is surprising that the volume of the light-emitting layer for our devices is smaller by 30 to 500 times than those of the other cases where a bright EL is visible to the eye. [11] [12] It will also be possible to reduce the operating voltage of our devices further and to increase EL efficiency by optimizing the device structure. For this purpose, the use of avalanche breakdown in a p+/NCs/n+ structure will be also effective. Thus, the LED that we demonstrated is a promising device to realize a monolithic optoelectronic ICs. In summary, we have fabricated LEDs with Schottky contacts on Si-NCs formed by a simple method. These LEDs give EL that can be seen with the naked eye at room temperature. The EL spectrum has a major peak of a photon energy of 1.9 eV and a minor peak of an energy of 2.2 eV. Since the electrons and holes for a radiative recombination are injected into the levels of nanocrystals through avalanche breakdown, the light emission voltage can be reduced to 4.0- 4.5 V, which is low enough to be applied by a standard Si device.

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FIG. 1. Cross-sectional scheme of the formed device.

FIG. 2. Cross sectional HR-TEM lattice image of the a-Si layers that ex perienced one minute's oxidation.

FIG. 3. I-V characteristic measured for a Si-NC device that experienced one minute of oxidation.

FIG. 4. EL spectra of a Si-NC device measured at room temperature under the reverse bias of 5.0V and the current of 60 mA.